

## PATENT ABSTRACTS OF JAPAN

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**(54) MARTENSITIC STAINLESS STEEL FOR OIL WELL**

**(57)Abstract:**

PROBLEM TO BE SOLVED: To allow this steel to exhibit corrosion resistance equal to or above that of duplex stainless steel even in an environment of carbon dioxide contg. hydrogen sulfide by allowing it to have a specified compsn. contg. C, Si, Mn, P, S, Cr, Mo, Ni, Co, sol.Al, N, O, Cu, W, and the balance Fe with inevitable impurities.

SOLUTION: This steel has a compsn. contg., by weight, 0.001 to 0.05% C, 0.05 to 1% Si, 0.05 to 2% Mn, &le;0.025% P, &le;0.01% S, 9 to 14% Cr, 3.1 to 7% Mo, 1 to 8% Ni, 0.5 to 7% Co, 0.001 to 0.1% sol.Al, &le;0.05% N, &le;0.01% O, 0 to 5% Cu, 0 to 5% W, and the balance Fe with inevitable impurities. The steel is formed into a slab by an ordinary ingot-making method or a continuous casting method, and the slab is hot-rolled to form into a product as it is, or, it is subjected to tempering or quenching and tempering after the hot rolling to form into a product. Preferably, the quenching is executed at 800 to 1,000°C, and the tempering is executed at 500 to 700°C.

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**TECHNICAL FIELD**

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[The technical field to which invention belongs] this invention is used for a steel pipe, an oil well well bottom hole device, a bulb, etc. the flow line which conveys the oil well pipe which pumps out the crude oil which contains carbon dioxide gas and hydrogen-sulfide gas in more detail, and its crude oil, and for line pipes about the martensitic stainless steel excellent in a carbon-dioxide-gas corrosive and sulfide-proof stress crack nature, and relates to the suitable martensitic stainless steel for oil wells.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] this invention was made in view of the above-mentioned actual condition, the purpose excels [ this invention ] the above-mentioned super 13Cr steel in corrosion resistance, for example, pH is 3 and is to provide the bottom of the carbon-dioxide-gas environment containing a hydrogen sulfide [ many / more / (0.05atm \*\*, 1 atm or less) ] with 2 phase stainless steel, and the corrosion resistance more than equivalent and the martensitic stainless steel for oil wells which specifically has a carbon-dioxide-gas corrosive and sulfide-proof stress crack nature.

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MEANS

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[Means for Solving the Problem] The summary of this invention is in the following martensitic stainless steel for oil wells.

[0007] By weight %, C:0.001 - 0.05%, Si:0.05-1%, Mn:0.05-2%, P:0.025% or less, S:0.01% or less, Cr:9-14%, Mo:3.1-7%, nickel: 1-8%, Co:0.5-7%, sol.aluminum:0.001-0.1%, The martensitic stainless steel for oil wells excellent in the carbon-dioxide-gas corrosive and sulfide-proof stress crack nature which N:0.05% or less, O (oxygen):0.01% or less, Cu:0-5%, and W:0 - 5% are contained, and the remainder becomes from Fe and an unescapable impurity.

[0008] The martensitic stainless steel for oil wells of the above-mentioned this invention In addition to the above-mentioned component, by weight %, V:0.001 - 0.5%, Nb:0.001-0.5%, one sort chosen from from while of Ti:0.001-0.5% and Zr:0.001-0.5% -- or further two or more sorts calcium: You may contain one sort chosen from from while of 0.0005-0.05%, Mg:0.0005-0.05%, and REM:0.0005-0.05%, or two sorts or more.

[0009] The above-mentioned this invention was completed based on the following knowledge.

[0010] It can arrange by the content of Cr and Mo, the corrosion resistance of the martensitic stainless steel under the carbon-dioxide-gas environment containing the hydrogen sulfide of a minute amount has especially the large influence of Mo content, and if Mo content is made [ many ], its corrosion resistance will improve sharply.

[0011] However, in a martensitic stainless steel, in order to avoid the selective corrosion resulting from 2 phase mixture organization which 2 phase stainless steel has, when making the organization into a martensite single phase organization aim, Mo content cannot be recklessly made [ many ]. Since Mo is a ferritizer, although, as for this, addition of austenite generation elements, such as nickel, is needed with the increase in Mo content, since addition of nickel etc. reduces the temperature (temperature = Ms point which a martensitic transformation starts) in which the austenite which is a parent phase carries out a martensitic transformation, it is because it is hard coming to generate martensite.

[0012] That is, if an Ms point falls and it becomes below a room temperature near the room temperature, it will become the organization which a martensitic transformation stops being able to happen easily and contains a retained-austenite phase so much. Intensity, especially yield strength fall and the steel which contains this retained-austenite phase so much cannot be used as steel for oil wells. Moreover, in order that intensity may change sharply by slight processing, the steel materials of uniform intensity are not obtained on manufacture.

[0013] Therefore, in order to improve corrosion resistance, in making [ many ] Mo content, in order to secure a martensite single phase organization, an austenite generation element is added, and the device conventionally maintained just like steel, without reducing an Ms point on it is needed.

[0014] For this reason, this invention persons did experiment research wholeheartedly, in order to find out many other properties, especially the austenite generation element which does not have a big bad influence on corrosion resistance for many elements it not only not to to reduce an Ms point, but.

[0015] Consequently, Co was an austenite generation element, it was made to go up about [ not reducing an Ms point ] or a little, and it became clear not to have a big bad influence on many other properties moreover.

[0016] Then, as a result of performing a component design in consideration of distribution of each element, and phase balance and control of an Ms point, the steel which has the above-mentioned chemical composition demonstrated 2 phase stainless steel and the corrosion resistance more than equivalent under the carbon-dioxide-gas environment containing a hydrogen sulfide [ that there is more much pH 3 (0.05atm \*\*, 1 atm or less) ], and, moreover, desired intensity carried out the knowledge of the ability to stabilize and secure.

[0017] In addition, as a low C martensitic stainless steel containing Co and Mo, there is steel shown in JP,59-15978,B, JP,4-268018,A, a 4-268019 official report, and a 8-246107 official report, for example. However, since Mo content of each steel shown in these official reports is 3% or less, the corrosion resistance is inferior to 2 phase stainless steel. Moreover, since Co is carried out to to 4.0% at the maximum, in such steel, this invention cannot solve the target technical problem.

[0018]

[Embodiments of the Invention] Hereafter, in this invention, the reason which limited the chemical composition of steel as mentioned above is explained in detail. In addition, "%" means "weight %" below.

[0019] C: If the content of C exceeds 0.05%, a degree of hardness with hardening becomes high, even if it carries out temper at an elevated temperature, intensity will not fall, but sulfide-proof stress crack nature will fall. Since the degree-of-hardness rise of a heat affected zone became remarkably large and toughness and corrosion resistance fell when using it especially, having welded, the upper limit was determined as 0.05%. In addition, although it is better as C content has the lower low one for it being good

and securing the toughness of a heat affected zone with welding especially, too much reduction causes a cost rise. For this reason, manufacture made the minimum 0.001% in consideration of the easy thing economically. The range of desirable C content is 0.001 - 0.025%, and the more desirable range is 0.001 - 0.01%.

[0020] Although Si:Si is an element required for the deoxidation of steel, since it is a ferritizer, if it adds too much, a delta ferrite will generate and corrosion resistance and hot-working nature will fall. However, in order to acquire sufficient deoxidation effect, 0.05% or more of content is required. On the other hand, if a content is carried out exceeding 1%, it will become easy to generate a ferrite. Therefore, Si content could be 0.05 - 1%.

[0021] Like the above-mentioned Si, Mn:Mn is required as a deoxidizer of steel, and is an element with the operation which raises hot-working nature. However, at less than 0.05%, those effects are not fully demonstrated for the content. On the other hand, if it is made to contain exceeding 2%, toughness will fall. For this reason, Mn content could be 0.05 - 2%.

[0022] P: P exists in steel as an unescapable impurity, and reduces corrosion resistance and toughness. In order to secure sufficient corrosion resistance and toughness, it is necessary to make the content 0.025% or less. In addition, as P content is low, it is better.

[0023] S: Like the above-mentioned P, S exists in steel as an unescapable impurity, and reduces hot-working nature, corrosion resistance, and toughness. In order to secure sufficient hot-working nature, corrosion resistance, and toughness, it is necessary to make the content 0.01% or less. In addition, like the above-mentioned P, as S content is low, it is better.

[0024] Although Cr:Cr is the corrosion resistance of a martensitic stainless steel, and a component which raises a carbon-dioxide-gas-proof corrosive especially, at less than 9%, an effect is not acquired for the content. On the other hand, if it is made to contain exceeding 14%, even if it will add Co mentioned later, an Ms point falls, a retained-austenite phase generates, it is still hardening and considering as martensite single phase becomes difficult. Therefore, Cr content could be 9 - 14%. In addition, since its carbon-dioxide-gas-proof corrosive improves the more the more Cr content is high, it is 10.5 - 14% preferably.

[0025] By making the content into 3.1% or more, it is an element important when securing the best sulfide-proof stress crack nature, and as a martensitic stainless steel, the highest sulfide-proof stress crack nature is secured, and the more Mo:Mo increases the content, the more the localized-corrosion nature under carbon-dioxide-gas environment and its sulfide-proof stress crack nature improve. however, if it is a powerful ferritizer and the content exceeds 7%, even if Mo adds Co of the amount mentioned later, a delta ferrite will generate it -- an Ms point both comes to fall For this reason, Mo content could be 3.1 - 7%.

[0026] nickel:nickel is the most important element in Co later mentioned when suppressing generation of a delta ferrite in the martensitic stainless steel of the low C-quantity Cr-quantity Mo of this invention. However, at less than 1%, even if the content makes the below-mentioned Co contain to upper-limit \*\*\*\*\*, it cannot inhibit generation of a delta ferrite. On the other hand, if it is made to contain exceeding 8%, an Ms point will fall and a retained-austenite phase will come to generate. Therefore, nickel content could be 1 - 8%. in addition, as the mould size at the time of continuous casting and the ingot size at the time of ingot making become large, it is better for nickel to make the content into 5 - 8% more desirably 3 to 8% at those with an operation which suppress the segregation of a segregation plain-gauze cone ferritizer, and the well which acquires this effect

[0027] Co:Co is an element in which an Ms point is not reduced, suppresses generation of the delta ferrite in the elevated temperature of the martensitic stainless steel of the low C-quantity Cr-quantity Mo of this invention, and when it cools, in order that it may not make a retained austenite generate, it is indispensable while it stabilizes an austenite phase at an elevated temperature. However, the content of the effect was not enough at less than 0.5%, and since it was an expensive element, 7% was made into the upper limit in consideration of the manufacturing cost.

[0028] The content is not obtained for \*\* by the element which needs sol.aluminum:aluminum as a deoxidizer of steel, and effect sufficient at less than 0.001% is not acquired with sol.aluminum. On the other hand, if it is made to contain exceeding 0.1%, since it is a powerful ferritizer, a delta ferrite will come to generate. Therefore, the sol.aluminum content could be 0.001 - 0.1%.

[0029] N: If N exists in steel as an unescapable impurity and the content exceeds 0.05%, a degree of hardness with hardening becomes high, even if it carries out temper at an elevated temperature, intensity will not fall, but sulfide-proof stress crack nature will fall. Since the degree-of-hardness rise of a heat affected zone became remarkably large and toughness and corrosion resistance fell when using it especially, having welded, the upper limit was determined as 0.05%. In addition, as N content is low, the toughness of a heat affected zone with welding becomes better. A desirable upper limit is 0.025% or less, and a more desirable upper limit is 0.010%.

[0030] O(oxygen): Since toughness and corrosion resistance fell when it existed in steel as an unescapable impurity and the content exceeded 0.01% like the above-mentioned N, O made the upper limit 0.01%.

[0031] Although it is not necessary to add, since a carbon-dioxide-gas-proof corrosive and sulfide-proof stress crack nature will improve if it adds, Cu:Cu can be added if needed. Although the effect becomes remarkable at 0.5% or more, if it is made to contain exceeding 5%, hot-working nature will deteriorate and the manufacture yield will fall. Therefore, as for Cu content in the case of adding, considering as 0.5 - 5% is good.

[0032] W: Although it is not necessary to add, since the localized-corrosion nature under carbon-dioxide-gas environment will improve if it adds, W can be added if needed. Although the effect becomes remarkable at 0.5% or more, if it is made to contain exceeding 5%, generation of a delta ferrite and the fall of an Ms point will take place. Therefore, as for W content in the case of adding, considering as 0.5 - 5% is good.

[0033] Although the steel of this invention is enough if it has the above-mentioned chemical composition, it may contain the following element.

[0034] V, Nb, Ti, and Zr: -- since it has the operation which each of these elements fixes C and makes dispersion in strong small



-- the need -- responding -- among these -- since -- one selected sort or two sorts or more can be added However, at less than 0.001%, the effect of the above [ the content ] is acquired for neither of the elements. On the other hand, if any element is made to contain exceeding 0.5%, a delta ferrite will generate and hot-working nature will fall. Therefore, each content of these elements in the case of adding could be 0.001 - 0.5%.

[0035] calcium, Mg, and rapid-eye-movement: -- since each of these elements raises the hot-working nature of steel and also it has the operation which prevents nozzle \*\*\*\*\* at the time of casting -- the need -- responding -- among these -- since -- one selected sort or two sorts or more can be added However, at less than 0.0005%, the effect of the above [ the content ] is acquired for neither of the elements. On the other hand, if it is made to contain over any element 0.05, a big and rough oxide will generate, it will become the origin of pitting, and corrosion resistance will fall. Therefore, each content of these elements in the case of adding could be 0.0005 - 0.05%.

[0036] The martensitic stainless steel for oil wells of this invention which has the above-mentioned chemical composition can be manufactured by ingoting using steel-manufacture furnaces, such as a converter and an electric furnace, refining the molten metal using refinement furnaces, such as an AOD furnace and a VOD furnace, if needed, considering as the cast piece of a size predetermined by the ingot making method or the continuous casting process subsequently, hot-rolling this cast piece, making a predetermined product configuration, and considering as a product as it is, or performing annealing or hardening tempering processing after rolling. What is necessary is for special processing to be unnecessary and just to manufacture it according to a conventional method in that case.

[0037] However, the temperature in the case of annealing 800-1000 degrees C of temperature in the case of hardening has desirable \*\*'s in 500-700 degrees C, reservation of the martensitic structure in which a martensite single phase organization or a little retained austenite exists in this case is attained, and also dispersion in strong becomes small as much as possible.

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PRIOR ART

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[Description of the Prior Art] The environment of the well for extracting petroleum or natural gas in recent years is still severer, and the corrosion of the oil well pipe which unearths a crude oil, and piping at the time of conveying a crude oil, without performing processing which suppresses corrosion poses a big problem from underground.

[0003] Conventionally, general carbon steel and a general inhibitor are used together to the oil wells which contain carbon dioxide gas so much, or 13Cr system martensitic stainless steel has been used for it. Moreover, the improvement steel called the super 13Cr steel with which not only carbon dioxide gas but pH reduced the carbon content in the oil well which contains the hydrogen sulfide of a minute amount (0.05 or less atms) by 3 is developed, and the use is being expanded.

[0004] However, in the environment where pH contains a hydrogen sulfide [ many / more / (0.05atm \*\*, 1 atm or less) ] by 3 like the above, there are no usable martensitic stainless steels including the above-mentioned improvement steel, and expensive 2 phase stainless steel had to be used. However, since 2 phase stainless steel has 2 phase organizations of a ferrite phase and an austenite phase, and a selective corrosion occurs or it makes the yield of an oil well increase, there is [ problems, like the corrosion rate in reed die JINGU which pours in an acid is remarkably large compared with a martensitic stainless steel ], and the scope is restricted.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] The martensitic stainless steel of this invention has the corrosion resistance in which expensive 2 phase stainless steel is excelled, though it is high intensity and high toughness. For this reason, conventionally, it can use for the portion by which use of 2 phase stainless steel was made indispensable, since it is high intensity, the thinning of a member can be attained, and there is little amount of the material used, and it is settled, and it attaches at a low price as a result compared with the case where 2 phase stainless steel is used. Moreover, lightweight-ization of device equipment can also be attained.

[0054] Moreover, not only a base material but the performance of a weld zone is good, and this invention steel is used not only for an oil well pipe but for uses used welding, such as a flow line and a line pipe, and is very effective.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]**

[0001]

[The technical field to which invention belongs] this invention is used for a steel pipe, an oil well well bottom hole device, a bulb, etc. the flow line which conveys the oil well pipe which pumps out the crude oil which contains carbon dioxide gas and hydrogen-sulfide gas in more detail, and its crude oil, and for line pipes about the martensitic stainless steel excellent in a carbon-dioxide-gas corrosive and sulfide-proof stress crack nature, and relates to the suitable martensitic stainless steel for oil wells.

[0002]

[Description of the Prior Art] The environment of the well for extracting petroleum or natural gas in recent years is still severer, and the corrosion of the oil well pipe which unearths a crude oil, and piping at the time of conveying a crude oil, without performing processing which suppresses corrosion poses a big problem from underground.

[0003] Conventionally, general carbon steel and a general inhibitor are used together to the oil wells which contain carbon dioxide gas so much, or 13Cr system martensitic stainless steel has been used for it. Moreover, the improvement steel called the super 13Cr steel with which not only carbon dioxide gas but pH reduced the carbon content in the oil well which contains the hydrogen sulfide of a minute amount (0.05 or less atms) by 3 is developed, and the use is being expanded.

[0004] However, in the environment where pH contains a hydrogen sulfide [ many / more / (0.05atm \*\*, 1 atm or less) ] by 3 like the above, there are no usable martensitic stainless steels including the above-mentioned improvement steel, and expensive 2 phase stainless steel had to be used. However, since 2 phase stainless steel has 2 phase organizations of a ferrite phase and an austenite phase, and a selective corrosion occurs or it makes the yield of an oil well increase, there is [ problems, like the corrosion rate in reed die JINGU which pours in an acid is remarkably large compared with a martensitic stainless steel ], and the scope is restricted.

[0005]

[Problem(s) to be Solved by the Invention] this invention was made in view of the above-mentioned actual condition, the purpose excels [ this invention ] the above-mentioned super 13Cr steel in corrosion resistance, for example, pH is 3 and is to provide the bottom of the carbon-dioxide-gas environment containing a hydrogen sulfide [ many / more / (0.05atm \*\*, 1 atm or less) ] with 2 phase stainless steel, and the corrosion resistance more than equivalent and the martensitic stainless steel for oil wells which specifically has a carbon-dioxide-gas corrosive and sulfide-proof stress crack nature.

[0006]

[Means for Solving the Problem] The summary of this invention is in the following martensitic stainless steel for oil wells.

[0007] By weight %, C:0.001 - 0.05%, Si:0.05-1%, Mn:0.05-2%, P:0.025% or less, S:0.01% or less, Cr:9-14%, Mo:3.1-7%, nickel: 1-8%, Co:0.5-7%, sol.aluminum:0.001-0.1%, The martensitic stainless steel for oil wells excellent in the carbon-dioxide-gas corrosive and sulfide-proof stress crack nature which N:0.05% or less, O (oxygen):0.01% or less, Cu:0-5%, and W:0 - 5% are contained, and the remainder becomes from Fe and an unescapable impurity.

[0008] The martensitic stainless steel for oil wells of the above-mentioned this invention In addition to the above-mentioned component, by weight %, V:0.001 - 0.5%, Nb:0.001-0.5%, one sort chosen from from while of Ti:0.001-0.5% and Zr:0.001-0.5% -- or further two or more sorts calcium: You may contain one sort chosen from from while of 0.0005-0.05%, Mg:0.0005-0.05%, and REM:0.0005-0.05%, or two sorts or more.

[0009] The above-mentioned this invention was completed based on the following knowledge.

[0010] It can arrange by the content of Cr and Mo, the corrosion resistance of the martensitic stainless steel under the carbon-dioxide-gas environment containing the hydrogen sulfide of a minute amount has especially the large influence of Mo content, and if Mo content is made [ many ], its corrosion resistance will improve sharply.

[0011] However, in a martensitic stainless steel, in order to avoid the selective corrosion resulting from 2 phase mixture organization which 2 phase stainless steel has, when making the organization into a martensite single phase organization aim, Mo content cannot be recklessly made [ many ]. Since Mo is a ferritizer, although, as for this, addition of austenite generation elements, such as nickel, is needed with the increase in Mo content, since addition of nickel etc. reduces the temperature (temperature = Ms point which a martensitic transformation starts) in which the austenite which is a parent phase carries out a martensitic transformation, it is because it is hard coming to generate martensite.

[0012] That is, if an Ms point falls and it becomes below a room temperature near the room temperature, it will become the

organization which a martensitic transformation stops being able to happen easily and contains a retained-austenite phase so much. Intensity, especially yield strength fall and the steel which contains this retained-austenite phase so much cannot be used as steel for oil wells. Moreover, in order that intensity may change sharply by slight processing, the steel materials of uniform intensity are not obtained on manufacture.

[0013] Therefore, in order to improve corrosion resistance, in making [ many ] Mo content, in order to secure a martensite single phase organization, an austenite generation element is added, and the device conventionally maintained just like steel, without reducing an Ms point on it is needed.

[0014] For this reason, this invention persons did experiment research wholeheartedly, in order to find out many other properties, especially the austenite generation element which does not have a big bad influence on corrosion resistance for many elements it not only not to to reduce an Ms point, but.

[0015] Consequently, Co was an austenite generation element, it was made to go up about [ not reducing an Ms point ] or a little, and it became clear not to have a big bad influence on many other properties moreover.

[0016] Then, as a result of performing a component design in consideration of distribution of each element, and phase balance and control of an Ms point, the steel which has the above-mentioned chemical composition demonstrated 2 phase stainless steel and the corrosion resistance more than equivalent under the carbon-dioxide-gas environment containing a hydrogen sulfide [ that there is more much pH 3 (0.05atm \*\*, 1 atm or less) ], and, moreover, desired intensity carried out the knowledge of the ability to stabilize and secure.

[0017] In addition, as a low C martensitic stainless steel containing Co and Mo, there is steel shown in JP,59-15978,B, JP,4-268018,A, a 4-268019 official report, and a 8-246107 official report, for example. However, since Mo content of each steel shown in these official reports is 3% or less, the corrosion resistance is inferior to 2 phase stainless steel. Moreover, since Co is carried out to to 4.0% at the maximum, in such steel, this invention cannot solve the target technical problem.

[0018]

[Embodiments of the Invention] Hereafter, in this invention, the reason which limited the chemical composition of steel as mentioned above is explained in detail. In addition, "%" means "weight %" below.

[0019] C: If the content of C exceeds 0.05%, a degree of hardness with hardening becomes high, even if it carries out temper at an elevated temperature, intensity will not fall, but sulfide-proof stress crack nature will fall. Since the degree-of-hardness rise of a heat affected zone became remarkably large and toughness and corrosion resistance fell when using it especially, having welded, the upper limit was determined as 0.05%. In addition, although it is better as C content has the lower low one for it being good and securing the toughness of a heat affected zone with welding especially, too much reduction causes a cost rise. For this reason, manufacture made the minimum 0.001% in consideration of the easy thing economically. The range of desirable C content is 0.001 - 0.025%, and the more desirable range is 0.001 - 0.01%.

[0020] Although Si:Si is an element required for the deoxidation of steel, since it is a ferritizer, if it adds too much, a delta ferrite will generate and corrosion resistance and hot-working nature will fall. However, in order to acquire sufficient deoxidation effect, 0.05% or more of content is required. On the other hand, if a content is carried out exceeding 1%, it will become easy to generate a ferrite. Therefore, Si content could be 0.05 - 1%.

[0021] Like the above-mentioned Si, Mn:Mn is required as a deoxidizer of steel, and is an element with the operation which raises hot-working nature. However, at less than 0.05%, those effects are not fully demonstrated for the content. On the other hand, if it is made to contain exceeding 2%, toughness will fall. For this reason, Mn content could be 0.05 - 2%.

[0022] P: P exists in steel as an unescapable impurity, and reduces corrosion resistance and toughness. In order to secure sufficient corrosion resistance and toughness, it is necessary to make the content 0.025% or less. In addition, if P content is low, it is as good as a low.

[0023] S: Like the above-mentioned P, S exists in steel as an unescapable impurity, and reduces hot-working nature, corrosion resistance, and toughness. In order to secure sufficient hot-working nature, corrosion resistance, and toughness, it is necessary to make the content 0.01% or less. In addition, like the above-mentioned P, if S content is low, it is as good as a low.

[0024] Although Cr:Cr is the corrosion resistance of a martensitic stainless steel, and a component which raises a carbon-dioxide-gas-proof corrosive especially, at less than 9%, an effect is not acquired for the content. On the other hand, if it is made to contain exceeding 14%, even if it will add Co mentioned later, an Ms point falls, a retained-austenite phase generates, it is still hardening and considering as martensite single phase becomes difficult. Therefore, Cr content could be 9 - 14%. In addition, since its carbon-dioxide-gas-proof corrosive improves the more the more Cr content is high, it is 10.5 - 14% preferably.

[0025] By making the content into 3.1% or more, it is an element important when securing the best sulfide-proof stress crack nature, and as a martensitic stainless steel, the highest sulfide-proof stress crack nature is secured, and the more Mo:Mo increases the content, the more the localized-corrosion nature under carbon-dioxide-gas environment and its sulfide-proof stress crack nature improve. however, if it is a powerful ferritizer and the content exceeds 7%, even if Mo adds Co of the amount mentioned later, a delta ferrite will generate it -- an Ms point both comes to fall For this reason, Mo content could be 3.1 - 7%.

[0026] nickel:nickel is the most important element in Co later mentioned when suppressing generation of a delta ferrite in the martensitic stainless steel of the low C-quantity Cr-quantity Mo of this invention. However, at less than 1%, even if the content makes the below-mentioned Co contain to upper-limit \*\*\*\*\*, it cannot inhibit generation of a delta ferrite. On the other hand, if it is made to contain exceeding 8%, an Ms point will fall and a retained-austenite phase will come to generate. Therefore, nickel content could be 1 - 8%. in addition, as the mould size at the time of continuous casting and the ingot size at the time of ingot making become large, it is better for nickel to make the content into 5 - 8% more desirably 3 to 8% at those with an operation



which suppress the segregation of a segregation plain-gauze cone ferritizer, and the well which acquires this effect

[0027] Co:Co is an element in which an Ms point is not reduced, suppresses generation of the delta ferrite in the elevated temperature of the martensitic stainless steel of the low C-quantity Cr-quantity Mo of this invention, and when it cools, in order that it may not make a retained austenite generate, it is indispensable while it stabilizes an austenite phase at an elevated temperature. However, the content of the effect was not enough at less than 0.5%, and since it was an expensive element, 7% was made into the upper limit in consideration of the manufacturing cost.

[0028] The content is not obtained for \*\* by the element which needs sol.aluminum:aluminum as a deoxidizer of steel, and effect sufficient at less than 0.001% is not acquired with sol.aluminum. On the other hand, if it is made to contain exceeding 0.1%, since it is a powerful ferritizer, a delta ferrite will come to generate. Therefore, the sol.aluminum content could be 0.001 - 0.1%.

[0029] N: If N exists in steel as an unescapable impurity and the content exceeds 0.05%, a degree of hardness with hardening becomes high, even if it carries out temper at an elevated temperature, intensity will not fall, but sulfide-proof stress crack nature will fall. Since degree-of-hardness elevation of a heat affected zone became remarkably large and toughness and corrosion resistance fell when using it especially, having welded, the upper limit was determined as 0.05%. In addition, if N content is low, in a low, the toughness of a heat affected zone with welding will become good. A desirable upper limit is 0.025% or less, and a more desirable upper limit is 0.010%.

[0030] O(oxygen): Since toughness and corrosion resistance fell when it existed in steel as an unescapable impurity and the content exceeded 0.01% like the above-mentioned N, O made the upper limit 0.01%.

[0031] Although it is not necessary to add, since a carbon-dioxide-gas-proof corrosive and sulfide-proof stress crack nature will improve if it adds, Cu:Cu can be added if needed. Although the effect becomes remarkable at 0.5% or more, if it is made to contain exceeding 5%, hot-working nature will deteriorate and the manufacture yield will fall. Therefore, as for Cu content in the case of adding, considering as 0.5 - 5% is good.

[0032] W: Although it is not necessary to add, since the localized-corrosion nature under carbon-dioxide-gas environment will improve if it adds, W can be added if needed. Although the effect becomes remarkable at 0.5% or more, if it is made to contain exceeding 5%, generation of a delta ferrite and the fall of an Ms point will take place. Therefore, as for W content in the case of adding, considering as 0.5 - 5% is good.

[0033] Although the steel of this invention is enough if it has the above-mentioned chemical composition, it may contain the following element.

[0034] V, Nb, Ti, and Zr: -- since it has the operation which each of these elements fixes C and makes dispersion in strong small -- the need -- responding -- among these -- since -- one selected sort or two sorts or more can be added However, at less than 0.001%, the effect of the above [ the content ] is acquired for neither of the elements. On the other hand, if any element is made to contain exceeding 0.5%, a delta ferrite will generate and hot-working nature will fall. Therefore, each content of these elements in the case of adding could be 0.001 - 0.5%.

[0035] calcium, Mg, and rapid-eye-movement: -- since each of these elements raises the hot-working nature of steel and also it has the operation which prevents nozzle \*\*\*\*\* at the time of casting -- the need -- responding -- among these -- since -- one selected sort or two sorts or more can be added However, at less than 0.0005%, the effect of the above [ the content ] is acquired for neither of the elements. On the other hand, if it is made to contain over any element 0.05, a big and rough oxide will generate, it will become the origin of pitting, and corrosion resistance will fall. Therefore, each content of these elements in the case of adding could be 0.0005 - 0.05%.

[0036] The martensitic stainless steel for oil wells of this invention which has the above-mentioned chemical composition can be manufactured by ingoting using steel-manufacture furnaces, such as a converter and an electric furnace, refining the molten metal using refinement furnaces, such as an AOD furnace and a VOD furnace, if needed, considering as the cast piece of a size predetermined by the ingot making method or the continuous casting process subsequently, hot-rolling this cast piece, making a predetermined product configuration, and considering as a product as it is, or performing annealing or hardening tempering processing after rolling. What is necessary is for special processing to be unnecessary and just to manufacture it according to a conventional method in that case.

[0037] However, the temperature in the case of annealing 800-1000 degrees C of temperature in the case of hardening has desirable \*\*'s in 500-700 degrees C, reservation of the martensitic structure in which a martensite single phase organization or a little retained austenite exists in this case is attained, and also dispersion in strong becomes small as much as possible.

[0038]

[Example] the cast piece which ingoted 40 kinds of steel which has the chemical composition shown in Table 1 and Table 2, and was obtained -- hot forging -- it hot-rolled and the plate for an examination with the thickness of 12mm, a width of face [ of 120mm ], and a length of 400mm was produced

[0039] Subsequently, the plates of two sheets which consist of each steel after performing hardening from 850 degrees C and tempering processing at 640 degrees C were arranged in the obtained plate in parallel with a rolling longitudinal direction, they were compared to it, gas tungsten arc welding of the comparison section was carried out to it using the welding materials which consist of 2 phase stainless steel of 25Cr system, and the welded joint was produced. At this time, the edge preparation whose angle is 45 degrees were performed to the comparison section. Moreover, welding is a heat gain 12 - 15 kJ/cm<sup>2</sup>. It carried out on conditions.

[0040]

[Table 1]

表 1

区分	No.	化 学 組 成 (重量%)														その他
		C	Si	Mn	P	S	Cr	Ni	Cu	Co	Mo	W	sol. Al	N	O	
本 発 明 例	1	0.006	0.34	0.76	0.011	0.001	12.1	3.5	-	4.7	4.9	-	0.015	0.002	0.004	-
	2	0.007	0.34	0.61	0.012	0.001	11.3	1.2	-	6.9	4.1	-	0.013	0.005	0.003	-
	3	0.006	0.31	0.33	0.015	0.001	12.5	3.0	-	6.3	4.8	-	0.012	0.004	0.003	-
	4	0.016	0.34	1.95	0.011	0.001	11.8	3.0	-	5.1	5.3	-	0.019	0.005	0.003	-
	5	0.008	0.24	0.51	0.015	0.001	11.7	5.8	-	3.9	4.2	-	0.018	0.002	0.003	-
	6	0.008	0.71	0.19	0.011	0.001	11.5	5.2	1.5	4.7	5.6	-	0.011	0.005	0.003	-
	7	0.010	0.24	0.55	0.012	0.001	12.4	4.1	-	5.6	3.7	2.3	0.018	0.006	0.005	-
	8	0.010	0.56	0.34	0.012	0.001	11.1	5.5	2.0	4.3	3.6	2.0	0.019	0.005	0.004	-
	9	0.004	0.63	0.40	0.011	0.001	13.1	5.0	-	3.1	4.3	-	0.019	0.006	0.003	V:0.05、Ti:0.08
	10	0.011	0.35	0.67	0.008	0.001	11.5	5.5	-	5.2	6.1	-	0.017	0.006	0.002	V:0.04、Ti:0.03
	11	0.009	0.25	0.57	0.010	0.001	12.7	4.0	-	5.0	4.1	-	0.012	0.001	0.004	Nb:0.02、Zr:0.12
	12	0.012	0.34	0.47	0.012	0.001	11.9	3.0	-	6.5	4.9	-	0.011	0.004	0.005	Ti:0.015
	13	0.019	0.65	1.27	0.015	0.001	12.5	4.8	-	6.8	5.8	-	0.010	0.002	0.003	Zr:0.22
	14	0.026	0.24	0.20	0.005	0.001	12.5	1.9	4.2	4.4	4.3	-	0.011	0.002	0.003	V:0.06、Zr:0.09
	15	0.025	0.59	1.08	0.016	0.001	13.2	4.5	-	5.8	3.9	1.2	0.013	0.006	0.005	Nb:0.025、Ti:0.018
	16	0.015	0.39	0.69	0.015	0.001	11.5	2.9	1.8	3.7	3.4	2.3	0.018	0.004	0.004	Ti:0.012
	17	0.010	0.29	1.10	0.015	0.001	11.5	2.8	-	5.0	4.2	-	0.016	0.003	0.004	Ca:0.0025
	18	0.012	0.25	0.58	0.011	0.001	12.7	4.8	-	3.1	4.3	-	0.017	0.009	0.004	Ca:0.0018、Mg:0.0012
	19	0.025	0.31	0.91	0.015	0.001	10.2	3.1	-	6.6	5.7	-	0.011	0.009	0.002	Ce:0.0021
	20	0.008	0.29	0.81	0.016	0.001	12.4	3.8	-	5.5	4.6	-	0.015	0.005	0.005	Mg:0.0037

注) 残部は、Feおよび不可避免的不純物である。

[0041]

[Table 2]

表 2

区分	No.	化 学 組 成 (重量%)														その他
		C	Si	Mn	P	S	Cr	Ni	Cu	Co	Mo	W	sol. Al	N	O	
本 発 明 例	21	0.042	0.29	0.60	0.014	0.001	12.7	5.7	-	6.7	6.1	-	0.016	0.006	0.002	Ca:0.0014、La:0.0021
	22	0.001	0.45	0.33	0.014	0.001	12.6	5.7	0.7	2.4	5.2	-	0.020	0.005	0.004	Ce:0.0044
	23	0.017	0.35	0.13	0.009	0.001	12.5	2.1	-	3.9	4.2	0.9	0.013	0.006	0.005	Mg:0.0027
	24	0.007	0.63	1.08	0.010	0.001	12.3	5.8	1.3	2.5	3.3	2.3	0.015	0.008	0.004	Ca:0.0032
	25	0.005	0.35	0.38	0.007	0.001	12.3	5.5	-	3.2	4.8	-	0.014	0.009	0.004	Ti:0.017、Ca:0.0014
	26	0.019	0.76	0.15	0.015	0.001	12.7	4.9	-	3.7	4.9	-	0.014	0.008	0.003	Ti:0.012、Ca:0.0014
	27	0.016	0.31	0.58	0.016	0.001	11.2	5.0	-	3.7	5.5	-	0.012	0.001	0.004	Ti:0.017、Ca:0.0011、Mg:0.0013
	28	0.018	0.45	0.48	0.013	0.001	10.3	5.7	-	2.5	4.1	-	0.011	0.009	0.003	V:0.07、Ti:0.087、Mg:0.0027
	29	0.026	0.34	0.59	0.022	0.001	12.1	5.7	-	4.6	5.7	-	0.013	0.007	0.005	Ti:0.014、Ca:0.0009
	30	0.015	0.05	1.09	0.015	0.001	12.5	2.1	2.2	4.7	4.6	-	0.017	0.005	0.003	Ti:0.019、Ca:0.0024
	31	0.006	0.31	0.25	0.004	0.001	11.8	4.1	-	5.4	3.7	2.1	0.010	0.011	0.004	Zr:0.027、Ca:0.0020
	32	0.012	0.24	0.67	0.015	0.001	9.5	3.0	0.7	5.9	4.5	1.3	0.014	0.002	0.004	Ti:0.012、Nb:0.011、Ce:0.0026
従 来 例	33	0.016	0.11	1.11	0.024	0.001	*22.2	5.0	-	*-	*2.6	-	0.014	*0.130	0.004	Ca:0.0019
	34	0.027	0.24	1.15	0.012	0.001	*21.9	5.2	-	*-	*2.4	-	0.011	*0.132	0.003	Ca:0.0023
	35	0.030	0.71	1.11	0.020	0.001	*20.0	4.9	-	*-	*2.3	-	0.012	*0.123	0.005	Ca:0.0027
比 較 例	36	0.006	0.91	0.25	0.015	0.001	12.0	5.5	-	*-	*2.1	-	0.011	0.007	0.004	Ca:0.0009
	37	0.016	0.33	1.21	0.013	0.001	10.1	5.9	-	*-	6.5	-	0.011	0.007	0.005	-
	38	0.008	0.17	1.08	0.011	0.001	13.5	*9.9	-	4.6	5.7	-	0.018	0.002	0.004	Ce:0.005
	39	*0.075	0.36	1.09	0.009	0.001	12.2	5.7	-	3.7	3.6	-	0.016	0.001	0.003	-
	40	0.010	0.55	1.34	0.015	0.001	11.9	5.5	-	3.2	4.2	-	0.018	*0.055	0.003	Mg:0.007

注1) 残部は、Feおよび不可避免的不純物である。

注2) \*印は、本発明で規定する範囲を外れることを示す。

[0042] And from the base material section of the obtained welded joint, the longitudinal direction extracted the round bar test piece for tensile test which are the diameter of 4mm of a rolling direction, and 20mm of distance between the gage marks, presented the tension test, and investigated proof stress (MPa) 0.2%.

[0043] Moreover, JISZ of the direction where a rolling direction and a longitudinal direction cross at right angles from the base material section and a weld zone The No. 4 test piece specified to 2202 was extracted, respectively, the Charpy impact test was

presented, and the fracture transition temperature  $vTrs$  (degree C) was investigated. In addition, the test piece from a weld zone was extracted so that the weld-junction section (boundary of the fused portion and the portion which is not fused) might be located in the V notch section.

[0044] Furthermore, from the base material section and the weld zone, the longitudinal direction extracted at a time two test pieces with the thickness of 2mm of the direction which intersects perpendicularly with a rolling direction, a width of face [ of 10mm ], and a length of 75mm for corrosion tests, respectively, presented the four-point bending stress grant corrosion-cracking examination of the following conditions, and investigated corrosion resistance (sulfide-proof stress crack nature). In addition, the test piece from a weld zone was extracted so that the above-mentioned weld-junction section might be located in the center of a longitudinal direction.

[0045] <<corrosion test condition>>

Testing liquid: 30atmCO<sub>2</sub>-0.1atmH<sub>2</sub>S saturation, 5%NaCl solution, \*\* Degree: 80-degree-C, load stress:base material proof stress [ 100% of ], and immersing time: 720 hours.

[0046] As for corrosion resistance evaluation, two test pieces made what non-\*\* "Ox" and both of generating of a crack were accepted a little in in that generating of a crack was accepted to be to one piece among fitness "OO" and two pieces in what generating of a crack was not accepted in non-\*\* "xx" by examination.

[0047] The above results of an investigation were collectively shown in Table 3.

[0048]

[Table 3]

表 3

区分	No	母材の特性			溶接熱影響部の特性	
		耐力 (MPa)	靱性 $vTrs$ (°C)	耐食性	靱性 $vTrs$ (°C)	耐食性
本 発 明 例	1	599	-76	○○	-51	○○
	2	620	-95	○○	-74	○○
	3	564	-93	○○	-64	○○
	4	561	-99	○○	-74	○○
	5	601	-87	○○	-63	○○
	6	625	-72	○○	-58	○○
	7	563	-72	○○	-51	○○
	8	581	-88	○○	-59	○○
	9	623	-78	○○	-62	○○
	10	569	-82	○○	-68	○○
	11	563	-91	○○	-80	○○
	12	589	-73	○○	-55	○○
	13	568	-96	○○	-83	○○
	14	625	-91	○○	-56	○○
	15	581	-102	○○	-88	○○
	16	630	-70	○○	-53	○○
	17	572	-74	○○	-52	○○
	18	615	-100	○○	-65	○○
	19	577	-77	○○	-67	○○
	20	612	-109	○○	-91	○○
	21	594	-71	○○	-56	○○
	22	574	-76	○○	-53	○○
	23	614	-89	○○	-77	○○
	24	603	-80	○○	-57	○○
	25	574	-98	○○	-63	○○
	26	571	-75	○○	-50	○○
	27	600	-72	○○	-51	○○
	28	588	-97	○○	-77	○○
	29	637	-70	○○	-55	○○
	30	577	-107	○○	-82	○○
	31	599	-81	○○	-56	○○
	32	635	-100	○○	-69	○○
従 来 例	33	515	-42	○○	-32	○×
	34	532	-55	○○	-37	○×
	35	522	-48	○×	-34	××
比 較 例	36	589	-108	××	-77	××
	37	493	-59	○×	-30	××
	38	461	<-110	○×	<-110	○×
	39	587	-71	○○	-15	××
	40	618	-92	○○	-11	××

[0049] As shown in Table 3, the steel of the example of this invention of No.1-32 had both the toughness of a base material and a weld zone, and good corrosion resistance, having the high intensity of 80ksi class (0.2% proof stress : 551 or more MPas) of API.

[0050] On the other hand, each of conventional steel (2 phase stainless steel) of No.33-35 had low intensity, and the corrosion resistance of steel was also inadequate and toughness is not only also inferior, but it was inferior in especially the corrosion



resistance of a weld zone.

[0051] Moreover, among the steel of the example of comparison of No.36-40 with which a chemical composition separates from the range specified by this invention, since intensity and toughness had few amounts of Mo of a good thing, the steel of No.36 was inferior to 2 phase stainless steel in corrosion resistance. The steel of No.37 had too many amounts of Mo, and also since Co was not included, the delta ferrite generated, and intensity and toughness were inferior not only in a low but corrosion resistance. Although the steel of No.38 contained Mo and Co of the amount specified by this invention, it separated from the upper limit of the range which the amount of nickel specifies by this invention, and the Ms point fell to eye a superfluous hatchet to near a room temperature. Consequently, there were many retained-austenite phases, the intensity of toughness of a very good thing was low, and it was inferior also in corrosion resistance. As for the steel of No.39-40, in addition to the thing with the very bad toughness of a weld zone of a good thing, the intensity of a base material, toughness, and corrosion resistance were [ the amount of C or N ] inferior to eye a superfluous hatchet also in corrosion resistance exceeding the upper limit of the range specified by this invention.

[0052] In addition, although the above-mentioned test result is the result of carrying out for a plate, even if test coupons are a steel pipe, shape steel, a steel bar, etc., it cannot be overemphasized by that the same result is obtained.

[0053]

[Effect of the Invention] The martensitic stainless steel of this invention has the corrosion resistance in which expensive 2 phase stainless steel is excelled, though it is high intensity and high toughness. For this reason, conventionally, it can use for the portion by which use of 2 phase stainless steel was made indispensable, since it is high intensity, the thinning of a member can be attained, and there is little amount of the material used, and it is settled, and it attaches at a low price as a result compared with the case where 2 phase stainless steel is used. Moreover, lightweight-ization of device equipment can also be attained.

[0054] Moreover, not only a base material but the performance of a weld zone is good, and this invention steel is used not only for an oil well pipe but for uses used welding, such as a flow line and a line pipe, and is very effective.

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[Translation done.]

\* NOTICES \*

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- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2. \*\*\*\* shows the word which can not be translated.
- 3. In the drawings, any words are not translated.

EXAMPLE

[Example] the cast piece which ingoted 40 kinds of steel which has the chemical composition shown in Table 1 and Table 2, and was obtained -- hot forging -- it hot-rolled and the plate for an examination with the thickness of 12mm, a width of face [ of 120mm ], and a length of 400mm was produced

[0039] Subsequently, the plates of two sheets which consist of each steel after performing hardening from 850 degrees C and tempering processing at 640 degrees C were arranged in the obtained plate in parallel with a rolling longitudinal direction, they were compared to it, gas tungsten arc welding of the comparison section was carried out to it using the welding materials which consist of 2 phase stainless steel of 25Cr system, and the welded joint was produced. At this time, the edge preparation whose angle is 45 degrees were performed to the comparison section. Moreover, welding is a heat gain 12 - 15 kJ/cm2. It carried out on conditions.

[0040]

[Table 1]

表 1

区分	No.	化 学 組 成 (重量%)														その他
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本 発 明 例	1	0.006	0.34	0.76	0.011	0.001	12.1	3.5	-	4.7	4.9	-	0.015	0.002	0.004	-
	2	0.007	0.34	0.61	0.012	0.001	11.3	1.2	-	6.9	4.1	-	0.013	0.005	0.003	-
	3	0.006	0.31	0.33	0.015	0.001	12.5	3.0	-	6.3	4.8	-	0.012	0.004	0.003	-
	4	0.016	0.34	1.95	0.011	0.001	11.8	3.0	-	5.1	5.3	-	0.019	0.005	0.003	-
	5	0.008	0.24	0.51	0.015	0.001	11.7	5.8	-	3.9	4.2	-	0.016	0.002	0.003	-
	6	0.008	0.71	0.19	0.011	0.001	11.5	5.2	1.5	4.7	5.6	-	0.011	0.005	0.003	-
	7	0.010	0.24	0.55	0.012	0.001	12.4	4.1	-	5.6	3.7	2.3	0.018	0.006	0.005	-
	8	0.010	0.58	0.34	0.012	0.001	11.1	5.5	2.0	4.3	3.6	2.0	0.019	0.005	0.004	-
	9	0.004	0.63	0.40	0.011	0.001	13.1	5.0	-	3.1	4.3	-	0.019	0.006	0.003	V:0.05、Ti:0.08
	10	0.011	0.35	0.67	0.008	0.001	11.5	5.5	-	5.2	6.1	-	0.017	0.006	0.002	V:0.04、Ti:0.03
	11	0.009	0.25	0.57	0.010	0.001	12.7	4.0	-	5.0	4.1	-	0.012	0.001	0.004	Nb:0.02、Zr:0.12
	12	0.012	0.34	0.47	0.012	0.001	11.9	3.0	-	6.5	4.9	-	0.011	0.004	0.005	Ti:0.015
	13	0.019	0.65	1.27	0.015	0.001	12.5	4.8	-	6.8	5.8	-	0.010	0.002	0.003	Zr:0.22
	14	0.026	0.24	0.20	0.005	0.001	12.5	1.9	4.2	4.4	4.3	-	0.011	0.002	0.003	V:0.06、Zr:0.09
	15	0.025	0.59	1.08	0.016	0.001	13.2	4.5	-	5.8	3.9	1.2	0.013	0.006	0.005	Nb:0.025、Ti:0.018
	16	0.015	0.39	0.69	0.015	0.001	11.5	2.9	1.8	3.7	3.4	2.3	0.018	0.004	0.004	Ti:0.012
	17	0.010	0.29	1.10	0.015	0.001	11.5	2.8	-	5.0	4.2	-	0.016	0.003	0.004	Ca:0.0025
	18	0.012	0.25	0.58	0.011	0.001	12.7	4.8	-	3.1	4.3	-	0.017	0.009	0.004	Ca:0.0018、Mg:0.0012
	19	0.025	0.31	0.91	0.015	0.001	10.2	3.1	-	6.6	5.7	-	0.011	0.009	0.002	Ce:0.0021
	20	0.008	0.29	0.81	0.016	0.001	12.4	3.8	-	5.5	4.6	-	0.015	0.005	0.005	Mg:0.0037

注) 残部は、Feおよび不可避免的不純物である。

[0041]

[Table 2]

表 2

区分	No	化 学 組 成 (重量%)														その他
		C	Si	Mn	P	S	Cr	Ni	Cu	Co	Mo	W	sol. Al	N	O	
本 発 明 例	21	0.042	0.29	0.60	0.014	0.001	12.7	5.7	-	6.7	6.1	-	0.016	0.006	0.002	Ca:0.0014、La:0.0021
	22	0.001	0.45	0.33	0.014	0.001	12.6	5.7	0.7	2.4	5.2	-	0.020	0.005	0.004	Ce:0.0044
	23	0.017	0.35	0.13	0.009	0.001	12.5	2.1	-	3.9	4.2	0.9	0.013	0.006	0.005	Mg:0.0027
	24	0.007	0.63	1.08	0.010	0.001	12.3	5.8	1.3	2.5	3.3	2.3	0.015	0.008	0.004	Ca:0.0032
	25	0.005	0.35	0.38	0.007	0.001	12.3	5.5	-	3.2	4.8	-	0.014	0.009	0.004	Ti:0.017、Ca:0.0014
	26	0.019	0.76	0.15	0.015	0.001	12.7	4.9	-	3.7	4.9	-	0.014	0.008	0.003	Ti:0.012、Ca:0.0014
	27	0.016	0.31	0.58	0.016	0.001	11.2	5.0	-	3.7	5.5	-	0.012	0.001	0.004	Ti:0.017、Ca:0.0011、Mg:0.0013
	28	0.018	0.45	0.48	0.013	0.001	10.3	5.7	-	2.5	4.1	-	0.011	0.009	0.003	V:0.07、Ti:0.087、Mg:0.0027
	29	0.026	0.34	0.59	0.022	0.001	12.1	5.7	-	4.6	5.7	-	0.013	0.007	0.005	Ti:0.014、Ca:0.0009
	30	0.015	0.05	1.09	0.015	0.001	12.5	2.1	2.2	4.7	4.6	-	0.017	0.005	0.003	Ti:0.019、Ca:0.0024
	31	0.006	0.31	0.25	0.004	0.001	11.8	4.1	-	5.4	3.7	2.1	0.010	0.011	0.004	Zr:0.027、Ca:0.0020
	32	0.012	0.24	0.67	0.015	0.001	9.5	3.0	0.7	5.9	4.5	1.3	0.014	0.002	0.004	Ti:0.012、Nb:0.011、Ce:0.0026
従 来 例	33	0.016	0.11	1.11	0.024	0.001	*22.2	5.0	-	*-	*2.6	-	0.014	*0.130	0.004	Ca:0.0019
	34	0.027	0.24	1.15	0.012	0.001	*21.9	5.2	-	*-	*2.4	-	0.011	*0.132	0.003	Ca:0.0023
	35	0.030	0.71	1.11	0.020	0.001	*20.0	4.9	-	*-	*2.3	-	0.012	*0.123	0.005	Ca:0.0027
比 較 例	36	0.006	0.91	0.25	0.015	0.001	12.0	5.5	-	*-	*2.1	-	0.011	0.007	0.004	Ca:0.0009
	37	0.016	0.33	1.21	0.013	0.001	10.1	5.9	-	*-	6.5	-	0.011	0.007	0.005	-
	38	0.008	0.17	1.08	0.011	0.001	13.5	*9.9	-	4.6	5.7	-	0.018	0.002	0.004	Ce:0.005
	39	*0.075	0.36	1.09	0.009	0.001	12.2	5.7	-	3.7	3.6	-	0.016	0.001	0.003	-
	40	0.010	0.55	1.34	0.015	0.001	11.9	5.5	-	3.2	4.2	-	0.018	*0.055	0.003	Mg:0.007

注1) 残部は、Feおよび不可避免の不純物である。  
注2) \*印は、本発明で規定する範囲を外れることを示す。

[0042] And from the base material section of the obtained welded joint, the longitudinal direction extracted the round bar test piece for tensile test which are the diameter of 4mm of a rolling direction, and 20mm of distance between the gage marks, presented the tension test, and investigated proof stress (MPa) 0.2%.

[0043] Moreover, JISZ of the direction where a rolling direction and a longitudinal direction cross at right angles from the base material section and a weld zone The No. 4 test piece specified to 2202 was extracted, respectively, the Charpy impact test was presented, and the fracture transition temperature vTrs (degree C) was investigated. In addition, the test piece from a weld zone was extracted so that the weld-junction section (boundary of the fused portion and the portion which is not fused) might be located in the V notch section.

[0044] Furthermore, from the base material section and the weld zone, the longitudinal direction extracted at a time two test pieces with the thickness of 2mm of the direction which intersects perpendicularly with a rolling direction, a width of face [ of 10mm ], and a length of 75mm for corrosion tests, respectively, presented the four-point bending stress grant corrosion-cracking examination of the following conditions, and investigated corrosion resistance (sulfide-proof stress crack nature). In addition, the test piece from a weld zone was extracted so that the above-mentioned weld-junction section might be located in the center of a longitudinal direction.

[0045] <<corrosion test condition>>  
Testing liquid: 30atmCO2-0.1atmH2S saturation, 5%NaCl solution, \*\* Degree: 80-degree-C, load stress:base material proof stress [ 100% of ], and immersing time: 720 hours.

[0046] corrosion resistance evaluation is good in what generating of a crack was not accepted for two test pieces in by examination -- what non-\*\* "Ox" and both of generating of a crack were accepted a little in in that generating of a crack was accepted to be to one piece among "OO" and two pieces was made into non-\*\* "xx"

[0047] The above results of an investigation were collectively shown in Table 3.

[0048]  
[Table 3]

表 3

区分	No	母材の特性			溶接熱影響部の特性	
		耐力 (MPa)	靱性 vTrs(℃)	耐食性	靱性 vTrs(℃)	耐食性
本 発 明 例	1	599	-76	○○	-51	○○
	2	620	-95	○○	-74	○○
	3	564	-93	○○	-64	○○
	4	561	-99	○○	-74	○○
	5	601	-87	○○	-63	○○
	6	625	-72	○○	-58	○○
	7	563	-72	○○	-51	○○
	8	581	-88	○○	-59	○○
	9	623	-78	○○	-62	○○
	10	569	-82	○○	-68	○○
	11	563	-91	○○	-80	○○
	12	589	-73	○○	-55	○○
	13	568	-96	○○	-83	○○
	14	625	-91	○○	-56	○○
	15	581	-102	○○	-88	○○
	16	630	-70	○○	-53	○○
	17	572	-74	○○	-52	○○
	18	615	-100	○○	-65	○○
	19	577	-77	○○	-67	○○
	20	612	-109	○○	-91	○○
	21	594	-71	○○	-56	○○
	22	574	-76	○○	-59	○○
	23	614	-89	○○	-77	○○
	24	603	-80	○○	-57	○○
	25	574	-98	○○	-69	○○
	26	571	-75	○○	-50	○○
	27	600	-72	○○	-51	○○
	28	588	-97	○○	-77	○○
	29	637	-70	○○	-55	○○
	30	577	-107	○○	-82	○○
	31	599	-81	○○	-56	○○
	32	635	-100	○○	-69	○○
従 来 例	33	515	-42	○○	-32	○×
	34	532	-55	○○	-37	○×
	35	522	-48	○×	-34	××
比 較 例	36	589	-108	××	-77	××
	37	493	-59	○×	-30	××
	38	461	<-110	○×	<-110	○×
	39	587	-71	○○	-15	××
	40	618	-92	○○	-11	××

[0049] As shown in Table 3, the steel of the example of this invention of No.1-32 had both the toughness of a base material and a weld zone, and good corrosion resistance, having the high intensity of 80ksi class (0.2% proof stress : 551 or more MPas) of API.

[0050] On the other hand, each of conventional steel (2 phase stainless steel) of No.33-35 had low intensity, and the corrosion resistance of steel was also inadequate and toughness is not only also inferior, but it was inferior in especially the corrosion resistance of a weld zone.

[0051] Moreover, among the steel of the example of comparison of No.36-40 with which a chemical composition separates from the range specified by this invention, since intensity and toughness had few amounts of Mo of a good thing, the steel of No.36 was inferior to 2 phase stainless steel in corrosion resistance. The steel of No.37 had too many amounts of Mo, and also since it did not contain Co, the delta ferrite generated it, and not only intensity and toughness are low, but it was inferior in corrosion resistance. Although the steel of No.38 contained Mo and Co of the amount specified by this invention, it separated from the upper limit of the range which the amount of nickel specifies by this invention, and the Ms point fell to eye a superfluous hatchet to near a room temperature. Consequently, there were many retained-austenite phases, the intensity of toughness of a very good thing was low, and it was inferior also in corrosion resistance. As for the steel of No.39-40, in addition to the thing with the very bad toughness of a weld zone of a good thing, the intensity of a base material, toughness, and corrosion resistance were [ the amount of C or N ] inferior to eye a superfluous hatchet also in corrosion resistance exceeding the upper limit of the range specified by this invention.

[0052] In addition, although the above-mentioned test result is the result of carrying out for a plate, even if test coupons are a steel pipe, shape steel, a steel bar, etc., it cannot be overemphasized by that the same result is obtained.

[Translation done.]

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] By weight %, C:0.001 - 0.05%, Si:0.05-1%, Mn:0.05-2%, P:0.025% or less, S:0.01% or less, Cr:9-14%, Mo:3.1-7%, nickel: 1-8%, Co:0.5-7%, sol.aluminum:0.001-0.1%, The martensitic stainless steel for oil wells excellent in the carbon-dioxide-gas corrosive and sulfide-proof stress crack nature which N:0.05% or less, O (oxygen):0.01% or less, Cu:0-5%, and W:0 - 5% are contained, and the remainder becomes from Fe and an unescapable impurity.

[Claim 2] Furthermore, the martensitic stainless steel for oil wells according to claim 1 which was excellent in weight % at the carbon-dioxide-gas corrosive and sulfide-proof stress crack nature containing one sort chosen from from while of V:0.001 - 0.5%, Nb:0.001-0.5%, Ti:0.001-0.5%, and Zr:0.001-0.5%, or two sorts or more.

[Claim 3] Furthermore, the martensitic stainless steel for oil wells according to claim 1 or 2 which was excellent in weight % at the carbon-dioxide-gas corrosive and sulfide-proof stress crack nature containing one sort chosen from from while of calcium:0.0005-0.05%, Mg:0.0005-0.05%, and REM:0.0005-0.05%, or two sorts or more.

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(54) 【発明の名称】 油井用マルテンサイト系ステンレス鋼

(57) 【要約】

【課題】 高価な2相ステンレス鋼に勝る耐硫化水素腐食性を有するマルテンサイト系ステンレス鋼を提供する。

【解決手段】 重量%で、C:0.001~0.05%、Si:0.05~1%、Mn:0.05~2%、P:0.025%以下、S:0.01%以下、Cr:9~14%、Mo:3.1~7%、Ni:1~8%、Co:0.5~7%、sol、Al:0.001~0.1%、N:0.05%以下、O:0.01%以下、Cu:0~5%、W:0~5%を含有し、残部がFeおよび不可避不純物からなるマルテンサイト系ステンレス鋼。

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(54)【発明の名称】 油井用マルテンサイト系ステンレス鋼

(57)【要約】  
【課題】高価な2相ステンレス鋼に勝る耐硫化水素腐食性を有するマルテンサイト系ステンレス鋼を提供する。  
【解決手段】重量%で、C:0.001~0.05%、Si:0.05~1%、Mn:0.05~2%、P:0.025%以下、S:0.01%以下、Cr:9~14%、Mo:3.1~7%、Ni:1~8%、Co:0.5~7%、sol. Al:0.001~0.1%、N:0.05%以下、O:0.01%以下、Cu:0~5%、W:0~5%を含有し、残部がF eおよび不可避不純物からなるマルテンサイト系ステンレス鋼。

## 【特許請求の範囲】

【請求項1】重量%で、C：0.001～0.05%、Si：0.05～1%、Mn：0.05～2%、P：0.025%以下、S：0.01%以下、Cr：9～14%、Mo：3.1～7%、Ni：1～8%、Co：0.5～7%、sol. Al：0.001～0.1%、N：0.05%以下、O（酸素）：0.01%以下、Cu：0～5%、W：0～5%を含有し、残部がFeおよび不可避不純物からなる炭酸ガス腐食性と耐硫化物応力割れ性に優れた油井用マルテンサイト系ステンレス鋼。 10

【請求項2】さらに、重量%で、V：0.001～0.5%、Nb：0.001～0.5%、Ti：0.001～0.5%およびZr：0.001～0.5%のうちから選ばれた1種または2種以上を含有する炭酸ガス腐食性と耐硫化物応力割れ性に優れた請求項1に記載の油井用マルテンサイト系ステンレス鋼。

【請求項3】さらに、重量%で、Ca：0.0005～0.05%、Mg：0.0005～0.05%およびREM：0.0005～0.05%のうちから選ばれた1種または2種以上を含有する炭酸ガス腐食性と耐硫化物 20 応力割れ性に優れた請求項1または請求項2に記載の油井用マルテンサイト系ステンレス鋼。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、炭酸ガス腐食性と耐硫化物応力割れ性に優れたマルテンサイト系ステンレス鋼に関し、より詳しくは炭酸ガスや硫化水素ガスを含む原油をくみ出す油井管やその原油を輸送するフローラインやラインパイプ用の鋼管、油井井戸坑底機器およびバルブなどに用いて好適な油井用マルテンサイト系ス 30 テンレス鋼に関する。

## 【0002】

【従来の技術】近年、石油または天然ガスを採取するための井戸の環境がますます過酷なものになっており、地中から原油を掘り出す油井管や、腐食を抑制する処理を行わずに原油を輸送する際の配管の腐食が、大きな問題となっている。

【0003】従来、炭酸ガスを多量に含む油井用には、一般の炭素鋼とインヒビターを併用したり、13Cr系マルテンサイトステンレス鋼が使用されてきた。また、 40 炭酸ガスだけでなく、例えば、pHが3で、微量（0.05atm以下）の硫化水素を含む油井では、炭素含有量を低減したスーパー13Cr鋼と称される改良鋼が開発され、その使用が拡大してきている。

【0004】ところが、上記と同様、pHが3で、より多く（0.05atm超、1atm以下）の硫化水素を含む環境では、上記の改良鋼を含めて使用可能なマルテンサイト系ステンレス鋼がなく、高価な2相ステンレス鋼を使用しなければならなかった。しかし、2相ステン 50 レス鋼は、フェライト相とオーステナイト相の2相組織

を有していることから、選択腐食が発生したり、油井の収量を増加させるために酸を注入するアシダイジングにおける腐食速度がマルテンサイト系ステンレス鋼に比べて著しく大きいなどの問題があり、適用範囲が限られている。

## 【0005】

【発明が解決しようとする課題】本発明は、上述の実状に鑑みなされたもので、その目的は、上記のスーパー13Cr鋼よりも耐食性に優れ、例えば、pHが3で、より多く（0.05atm超、1atm以下）の硫化水素を含む炭酸ガス環境下においても、2相ステンレス鋼と同等以上の耐食性、具体的には炭酸ガス腐食性と耐硫化物応力割れ性を有する油井用マルテンサイト系ステンレス鋼を提供することにある。

## 【0006】

【課題を解決するための手段】本発明の要旨は、下記の油井用マルテンサイト系ステンレス鋼にある。

【0007】重量%で、C：0.001～0.05%、Si：0.05～1%、Mn：0.05～2%、P：0.025%以下、S：0.01%以下、Cr：9～14%、Mo：3.1～7%、Ni：1～8%、Co：0.5～7%、sol. Al：0.001～0.1%、N：0.05%以下、O（酸素）：0.01%以下、Cu：0～5%、W：0～5%を含有し、残部がFeおよび不可避不純物からなる炭酸ガス腐食性および耐硫化物 応力割れ性に優れた油井用マルテンサイト系ステンレス鋼。

【0008】上記本発明の油井用マルテンサイト系ステンレス鋼は、上記の成分以外に、重量%で、V：0.001～0.5%、Nb：0.001～0.5%、Ti：0.001～0.5%およびZr：0.001～0.5%のうちから選ばれた1種または2種以上、さらには、Ca：0.0005～0.05%、Mg：0.0005～0.05%およびREM：0.0005～0.05%のうちから選ばれた1種または2種以上を含有するものであってもよい。

【0009】上記の本発明は、下記の知見に基づいて完成させた。

【0010】微量の硫化水素を含む炭酸ガス環境下におけるマルテンサイト系ステンレス鋼の耐食性は、CrとMoの含有量で整理でき、特にMo含有量の影響が大きく、Mo含有量を多くすれば耐食性が大幅に向上する。

【0011】しかし、2相ステンレス鋼が有する2相混合組織に起因する選択腐食をさけるために、マルテンサイト系ステンレス鋼においても、その組織をマルテンサイト単相組織狙いにする場合には、Mo含有量をむやみに多くすることはできない。これは、Moがフェライト生成元素であるので、Mo含有量の増加に伴ってNiなどのオーステナイト生成元素の添加が必要になるが、Niなどの添加は高温相であるオーステナイトがマルテン 50

サイト変態する温度（マルテンサイト変態が開始する温度＝Ms点）を低下させるので、マルテンサイトが生成しにくくなるためである。

【0012】すなわち、Ms点が低下し、室温近傍または室温以下になると、マルテンサイト変態が起こりなくなり、残留オーステナイト相を多量に含む組織になる。この残留オーステナイト相を多量に含む鋼は、強度、特に降伏強度が低下して油井用鋼として使用できない。また、わずかの加工で強度が大幅に変化するために、製造上均一な強度の鋼材が得られない。

【0013】したがって、耐食性を改善するためにMo含有量を多くする場合には、マルテンサイト単相組織を確保するためにオーステナイト生成元素を添加し、その上でMs点を低下させずに従来鋼なみに維持させる工夫が必要になる。

【0014】このため、本発明者らは、多くの元素を対象に、Ms点を低下させないだけでなく、その他の諸性質、特に耐食性に大きな悪影響を及ぼさないオーステナイト生成元素を見いだすために、鋭意実験研究を行った。

【0015】その結果、Coはオーステナイト生成元素であり、Ms点を低下させないばかりか若干上昇させ、しかもその他の諸性質に大きな悪影響を及ぼさないことが判明した。

【0016】そこで、各元素の配分と相バランス、Ms点のコントロールを考慮して成分設計を行った結果、上記の化学組成を有する鋼が、例えば、pHが3で、より多く（0.05atm超、1atm以下）の硫化水素を含む炭酸ガス環境下において2相ステンレス鋼と同等以上の耐食性を発揮し、しかも所望の強度が安定して確保できることを知見した。

【0017】なお、CoとMoを含む低Cマルテンサイト系ステンレス鋼としては、例えば、特公昭59-15978号公報、特開平4-268018号公報、同4-268019号公報および同8-246107号公報に示される鋼がある。しかし、これらの公報に示されている鋼は、いずれもMo含有量が3%以下であるので、その耐食性は2相ステンレス鋼よりも劣っている。また、Coは、最大で4.0%までとされているため、これらの鋼では本発明が対象としている課題を解決することができない。

【0018】

【発明の実施の形態】以下、本発明において、鋼の化学組成を上記のように限定した理由について詳細に説明する。なお、以下において、「%」は「重量%」を意味する。

【0019】C：Cの含有量が0.05%を超えると、焼入れままの硬度が高くなり、高温で焼戻しても強度が下がり、耐硫化物応力割れ性が低下する。特に、溶接して使用する場合には、溶接熱影響部の硬度上昇が著し

く大きくなり、靱性、耐食性が低下するので、その上限を0.05%と定めた。なお、C含有量は低い方がよく、特に溶接ままでの熱影響部の靱性を確保するには低ければ低いほどよいが、過度の低減はコスト上昇を招く。このため、経済的に製造が容易なことを考慮し、その下限を0.001%とした。好ましいC含有量の範囲は0.001～0.025%、より好ましい範囲は0.001～0.01%である。

【0020】Si：Siは鋼の脱酸に必要な元素であるが、フェライト生成元素であるので添加しすぎるとδフェライトが生成して耐食性、熱間加工性が低下する。しかし、十分な脱酸効果を得るためには0.05%以上の含有量が必要である。一方、1%を超えて含有量させると、フェライトが生成しやすくなる。したがって、Si含有量は0.05～1%とした。

【0021】Mn：Mnは、上記のSiと同様に、鋼の脱酸剤として必要であり、また熱間加工性を向上させる作用を持つ元素である。しかし、その含有量が0.05%未満ではそれらの効果が十分に発揮されない。一方、2%を超えて含有させると、靱性が低下する。このため、Mn含有量は0.05～2%とした。

【0022】P：Pは不可避不純物として鋼中に存在し、耐食性、靱性を低下させる。十分な耐食性、靱性を確保するためにはその含有量を0.025%以下にする必要がある。なお、P含有量は低ければ低いほどよい。

【0023】S：Sは、上記のPと同様に、不可避不純物として鋼中に存在し、熱間加工性、耐食性、靱性を低下させる。十分な熱間加工性、耐食性、靱性を確保するためにはその含有量を0.01%以下にする必要がある。なお、S含有量は、上記のPと同様に、低ければ低いほどよい。

【0024】Cr：Crは、マルテンサイト系ステンレス鋼の耐食性、なかでも耐炭酸ガス腐食性を向上させる成分であるが、その含有量が9%未満では効果が得られない。一方、14%を超えて含有させると、後述するCoを添加してもMs点が低下して残留オーステナイト相が生成し、焼入れままでマルテンサイト単相とすることが難しくなる。したがって、Cr含有量は9～14%とした。なお、Cr含有量は高ければ高いほど耐炭酸ガス腐食性が向上するので、好ましくは10.5～14%である。

【0025】Mo：Moは最良の耐硫化物応力割れ性を確保するうえで重要な元素であり、その含有量を3.1%以上とすることによって、マルテンサイト系ステンレス鋼としては最高の耐硫化物応力割れ性が確保され、その含有量を増せば増すほど炭酸ガス環境下での局部腐食性、耐硫化物応力割れ性が向上する。しかし、Moは強力なフェライト生成元素であり、その含有量が7%を超えると、後述する量のCoを添加してもδフェライトが生成するとともに、Ms点が低下するようになる。このた



め、Mo含有量は3.1~7%とした。

【0026】Ni: Niは、本発明の低C-高Cr-高Moのマルテンサイト系ステンレス鋼において、 $\delta$ フェライトの生成を抑制するうえで後述するCoとともに最も重要な元素である。しかし、その含有量が1%未満では、後述のCoを上限值いっぱいまで含有させても $\delta$ フェライトの生成を抑止できない。一方、8%を超えて含有させると、Ms点が低下して残留オーステナイト相が生成するようになる。したがって、Ni含有量は1~8%とした。なお、Niには、連続鍛造時のモールド寸法や造塊時のインゴット寸法が大きくなればなるほど偏析しやすいフェライト生成元素の偏析を抑制する作用あり、この効果を得るためにはその含有量を3~8%、より望ましくは5~8%とするのがよい。

【0027】Co: Coは、高温でオーステナイト相を安定化させるとともに、Ms点を低下させない元素であり、本発明の低C-高Cr-高Moのマルテンサイト系ステンレス鋼の高温での $\delta$ フェライトの生成を抑制し、冷却したときに残留オーステナイトを生成させないために必要不可欠である。しかし、その含有量が0.5%未満ではその効果が十分でなく、高価な元素であるので製造コストを考慮して7%を上限とした。

【0028】sol. Al: Alは鋼の脱酸剤として必要な元素だが、その含有量がsol. Alで0.001%未満では十分な効果が得られない。一方、0.1%を超えて含有させると、強力なフェライト生成元素であることから、 $\delta$ フェライトが生成するようになる。したがって、sol. Al含有量は0.001~0.1%とした。

【0029】N: Nは不可避的不純物として鋼中に存在し、その含有量が0.05%を超えると、焼入れままの硬度が高くなり、高温で焼戻しても強度が下がらず、耐硫化物応力割れ性が低下する。特に、溶接して使用する場合には、溶接熱影響部の硬度上昇が著しく大きくなり、靱性、耐食性が低下するので、その上限を0.05%と定めた。なお、N含有量は低ければ低いほど、溶接ままでの熱影響部の靱性が良好になる。好ましい上限は0.025%以下、より好ましい上限は0.010%である。

【0030】O(酸素): Oは、上記のNと同様に、不可避的不純物として鋼中に存在し、その含有量が0.01%を超えると、靱性、耐食性が低下するので、その上限を0.01%とした。

【0031】Cu: Cuは添加しなくてもよいが、添加すれば耐炭酸ガス腐食性、耐硫化物応力割れ性が向上するので、必要に応じて添加することができる。その効果は0.5%以上で顕著になるが、5%を超えて含有させると熱間加工性が劣化して製造歩留まりが低下する。したがって、添加する場合のCu含有量は0.5~5%とするのがよい。

【0032】W: Wは添加しなくてもよいが、添加すれば炭酸ガス環境下での局部腐食性が向上するので、必要に応じて添加することができる。その効果は0.5%以上で顕著になるが、5%を超えて含有させると、 $\delta$ フェライトの生成とMs点の低下が起こる。したがって、添加する場合のW含有量は0.5~5%とするのがよい。

【0033】本発明の鋼は、上記の化学組成を有すれば十分であるが、下記の元素を含むものであってもよい。

【0034】V、Nb、Ti、Zr: これらの元素は、いずれもCを固定し、強度のばらつきを小さくする作用を有するので、必要に応じて、これらのうちから選んだ1種または2種以上を添加することができる。しかし、いずれの元素もその含有量が0.001%未満では前記の効果が得られない。一方、いずれの元素も0.5%を超えて含有させると、 $\delta$ フェライトが生成して熱間加工性が低下する。したがって、添加する場合のこれら元素の含有量は、いずれも0.001~0.5%とした。

【0035】Ca、Mg、REM: これらの元素は、いずれも鋼の熱間加工性を向上させるほか、鍛造時のノズルづまりを防止する作用を有するので、必要に応じて、これらのうちから選んだ1種または2種以上を添加することができる。しかし、いずれの元素もその含有量が0.0005%未満では前記の効果が得られない。一方、いずれの元素も0.05%を超えて含有させると、粗大な酸化物が生成し、孔食の起点となって耐食性が低下する。したがって、添加する場合のこれら元素の含有量は、いずれも0.0005~0.05%とした。

【0036】上記の化学組成を有する本発明の油井用マルテンサイト系ステンレス鋼は、転炉や電気炉などの製鋼炉を用いて溶製し、必要に応じてその溶湯をAOD炉やVOD炉などの精錬炉を用いて精錬し、次いで造塊法や連続鍛造法で所定の大きさの鋳片とし、この鋳片を熱間圧延して所定の製品形状に仕上げ、そのまま製品とするか、圧延後に焼戻しまたは焼入れ焼戻し処理を施すことで製造できる。その際、特別な処理は不要で、常法に従って製造すればよい。

【0037】ただし、焼入れする場合の温度は800~1000℃、焼戻しする場合の温度は500~700℃とするのが好ましく、この場合にはマルテンサイト単相組織または少量の残留オーステナイトが存在するにすぎないマルテンサイト組織の確保が可能になるほか、強度のばらつきが可及的に小さくなる。

【0038】

【実施例】表1と表2に示す化学組成を有する40種類の鋼を溶製し、得られた鋳片を熱間鍛造、熱間圧延して厚さ12mm、幅120mm、長さ400mmの試験用板材を作製した。

【0039】次いで、得られた板材に、850℃からの焼入れと640℃での焼戻し処理を施した後、各鋼からなる2枚の板材同士を圧延長手方向に平行に並べて突き



合わせ、その突き合わせ部を25Cr系の2相ステンレス鋼からなる溶接材料を用いてガス・タングステン・アーク溶接し、溶接継手を作製した。この時、突き合わせ部には、角度が45°の開先加工を施した。また、溶接\*

\*は、入熱量12~15kJ/cm<sup>2</sup>の条件で行った。

【0040】

【表1】

表 1

区分	No.	化 学 組 成 (重量%)														その他
		C	Si	Mn	P	S	Cr	Ni	Cu	Co	Mo	W	sol. Al	N	O	
本発明例	1	0.006	0.34	0.76	0.011	0.001	12.1	3.5	-	4.7	4.9	-	0.015	0.002	0.004	-
	2	0.007	0.34	0.61	0.012	0.001	11.3	1.2	-	6.9	4.1	-	0.013	0.005	0.003	-
	3	0.006	0.31	0.33	0.015	0.001	12.5	3.0	-	6.3	4.8	-	0.012	0.004	0.003	-
	4	0.016	0.34	1.95	0.011	0.001	11.8	3.0	-	5.1	5.3	-	0.019	0.005	0.003	-
	5	0.008	0.24	0.51	0.015	0.001	11.7	5.8	-	3.9	4.2	-	0.016	0.002	0.003	-
	6	0.008	0.71	0.19	0.011	0.001	11.5	5.2	1.5	4.7	5.6	-	0.011	0.005	0.003	-
	7	0.010	0.24	0.55	0.012	0.001	12.4	4.1	-	5.6	3.7	2.3	0.018	0.006	0.005	-
	8	0.010	0.58	0.34	0.012	0.001	11.1	5.5	2.0	4.3	3.6	2.0	0.019	0.005	0.004	-
	9	0.004	0.63	0.40	0.011	0.001	13.1	5.0	-	3.1	4.3	-	0.019	0.006	0.003	V:0.05、Ti:0.08
	10	0.011	0.35	0.67	0.008	0.001	11.5	5.5	-	5.2	6.1	-	0.017	0.006	0.002	V:0.04、Ti:0.03
	11	0.009	0.25	0.57	0.010	0.001	12.7	4.0	-	5.0	4.1	-	0.012	0.001	0.004	Nb:0.02、Zr:0.12
	12	0.012	0.34	0.47	0.012	0.001	11.9	3.0	-	6.5	4.9	-	0.011	0.004	0.005	Ti:0.015
	13	0.019	0.65	1.27	0.015	0.001	12.5	4.8	-	6.8	5.8	-	0.010	0.002	0.003	Zr:0.22
	14	0.026	0.24	0.20	0.005	0.001	12.5	1.9	4.2	4.4	4.3	-	0.011	0.002	0.003	V:0.06、Zr:0.09
	15	0.025	0.59	1.08	0.016	0.001	13.2	4.5	-	5.8	3.9	1.2	0.013	0.006	0.005	Nb:0.025、Ti:0.018
	16	0.015	0.39	0.69	0.015	0.001	11.5	2.9	1.8	3.7	3.4	2.3	0.018	0.004	0.004	Ti:0.012
	17	0.010	0.29	1.10	0.015	0.001	11.5	2.8	-	5.0	4.2	-	0.016	0.003	0.004	Ca:0.0025
	18	0.012	0.25	0.58	0.011	0.001	12.7	4.8	-	3.1	4.3	-	0.017	0.009	0.004	Ca:0.0018、Mg:0.0012
	19	0.025	0.31	0.91	0.015	0.001	10.2	3.1	-	6.6	5.7	-	0.011	0.009	0.002	Ce:0.0021
	20	0.008	0.29	0.81	0.016	0.001	12.4	3.8	-	5.5	4.6	-	0.015	0.005	0.005	Mg:0.0037

注) 残部は、Feおよび不可避免的不純物である。

【0041】

※ ※【表2】

表 2

区分	No.	化 学 組 成 (重量%)														その他
		C	Si	Mn	P	S	Cr	Ni	Cu	Co	Mo	W	sol. Al	N	O	
本発明例	21	0.042	0.29	0.60	0.014	0.001	12.7	5.7	-	6.7	6.1	-	0.016	0.006	0.002	Ca:0.0014、La:0.0021
	22	0.001	0.45	0.33	0.014	0.001	12.6	5.7	0.7	2.4	5.2	-	0.020	0.005	0.004	Ce:0.0044
	23	0.017	0.35	0.13	0.009	0.001	12.5	2.1	-	3.9	4.2	0.9	0.013	0.006	0.005	Mg:0.0027
	24	0.007	0.63	1.08	0.010	0.001	12.3	5.8	1.3	2.5	3.3	2.3	0.015	0.008	0.004	Ca:0.0032
	25	0.005	0.35	0.38	0.007	0.001	12.3	5.5	-	3.2	4.8	-	0.014	0.009	0.004	Ti:0.017、Ca:0.0014
	26	0.019	0.76	0.15	0.015	0.001	12.7	4.9	-	3.7	4.9	-	0.014	0.008	0.003	Ti:0.012、Ca:0.0014
	27	0.016	0.31	0.58	0.016	0.001	11.2	5.0	-	3.7	5.5	-	0.012	0.001	0.004	Ti:0.017、Ca:0.0011、Mg:0.0013
	28	0.018	0.45	0.48	0.013	0.001	10.3	5.7	-	2.5	4.1	-	0.011	0.009	0.003	V:0.07、Ti:0.087、Mg:0.0027
	29	0.026	0.34	0.59	0.022	0.001	12.1	5.7	-	4.6	5.7	-	0.013	0.007	0.005	Ti:0.014、Ca:0.0009
	30	0.015	0.05	1.09	0.015	0.001	12.5	2.1	2.2	4.7	4.6	-	0.017	0.005	0.003	Ti:0.019、Ca:0.0024
	31	0.006	0.31	0.25	0.004	0.001	11.8	4.1	-	5.4	3.7	2.1	0.010	0.011	0.004	Zr:0.027、Ca:0.0020
	32	0.012	0.24	0.67	0.015	0.001	9.5	3.0	0.7	5.9	4.5	1.3	0.014	0.002	0.004	Ti:0.012、Nb:0.011、Ce:0.0026
従来例	33	0.016	0.11	1.11	0.024	0.001	*22.2	5.0	-	*-	*2.6	-	0.014	*0.130	0.004	Ca:0.0019
	34	0.027	0.24	1.15	0.012	0.001	*21.9	5.2	-	*-	*2.4	-	0.011	*0.132	0.003	Ca:0.0023
	35	0.030	0.71	1.11	0.020	0.001	*20.0	4.9	-	*-	*2.3	-	0.012	*0.123	0.005	Ca:0.0027
比較例	36	0.006	0.91	0.25	0.015	0.001	12.0	5.5	-	*-	*2.1	-	0.011	0.007	0.004	Ca:0.0009
	37	0.016	0.33	1.21	0.013	0.001	10.1	5.9	-	*-	6.5	-	0.011	0.007	0.005	-
	38	0.008	0.17	1.08	0.011	0.001	13.5	*9.9	-	4.6	5.7	-	0.018	0.002	0.004	Ce:0.005
	39	*0.075	0.36	1.09	0.009	0.001	12.2	5.7	-	3.7	3.6	-	0.016	0.001	0.003	-
	40	0.010	0.55	1.34	0.015	0.001	11.9	5.5	-	3.2	4.2	-	0.016	*0.055	0.003	Mg:0.007

注1) 残部は、Feおよび不可避免的不純物である。

注2) \*印は、本発明で規定する範囲を外れることを示す。

【0042】そして、得られた溶接継手の母材部から、長手方向が圧延方向の直径4mm、標点間距離20mmの丸棒引張試験片を採取して引張試験に供し、0.2%耐力(MPa)を調べた。

★【0043】また、母材部と溶接部とから、長手方向が圧延方向と直交する方向のJISZ 2202に規定される4号試験片をそれぞれ採取してシャルピー衝撃試験

★50 に供し、破面遷移温度vTrs(℃)を調べた。なお、

溶接部からの試験片は、溶接ボンド部（溶融した部分と溶融していない部分の境界）がVノッチ部に位置するように採取した。

【0044】さらに、母材部と溶接部とから、長手方向が圧延方向と直交する方向の厚さ2mm、幅10mm、長さ75mmの腐食試験用の試験片をそれぞれ2個ずつ採取し、下記条件の4点曲げ応力付与腐食割れ試験に供し、耐食性（耐硫化物応力割れ性）を調べた。なお、溶接部からの試験片は、上記の溶接ボンド部が長手方向の中央に位置するように採取した。

【0045】《腐食試験条件》

試験溶液：30atmCO<sub>2</sub>-0.1atmH<sub>2</sub>S飽和、5%NaCl水溶液、

\*温度：80℃、

負荷応力：母材耐力の100%、

浸漬時間：720時間。

【0046】耐食性の評価は、試験により、2個の試験片ともに割れの発生が認められなかったものを良好「○」、2個中1個に割れの発生が認められたものをやや不芳「○×」、2個ともに割れの発生が認められたものを不芳「××」とした。

【0047】以上の調査結果を、表3にまとめて示した。

【0048】

【表3】

区分	No.	母材の特性			溶接熱影響部の特性	
		耐力 (MPa)	靱性 vTrs(℃)	耐食性	靱性 vTrs(℃)	耐食性
本 発 明 例	1	599	-76	○○	-51	○○
	2	620	-95	○○	-74	○○
	3	564	-93	○○	-64	○○
	4	561	-99	○○	-74	○○
	5	601	-87	○○	-63	○○
	6	625	-72	○○	-58	○○
	7	563	-72	○○	-51	○○
	8	581	-88	○○	-59	○○
	9	623	-78	○○	-62	○○
	10	569	-82	○○	-68	○○
	11	563	-91	○○	-80	○○
	12	589	-73	○○	-55	○○
	13	568	-96	○○	-83	○○
	14	625	-91	○○	-56	○○
	15	581	-102	○○	-88	○○
	16	630	-70	○○	-53	○○
	17	572	-74	○○	-52	○○
	18	615	-100	○○	-65	○○
	19	577	-77	○○	-67	○○
	20	612	-109	○○	-91	○○
	21	594	-71	○○	-56	○○
	22	574	-76	○○	-63	○○
	23	614	-89	○○	-77	○○
	24	603	-80	○○	-57	○○
	25	574	-98	○○	-63	○○
	26	571	-75	○○	-50	○○
	27	600	-72	○○	-51	○○
	28	588	-97	○○	-77	○○
	29	637	-70	○○	-55	○○
	30	577	-107	○○	-82	○○
	31	599	-81	○○	-56	○○
	32	635	-100	○○	-69	○○
従 来 例	33	515	-42	○○	-32	○×
	34	532	-55	○○	-37	○×
	35	522	-48	○×	-34	××
比 較 例	36	589	-108	××	-77	××
	37	493	-59	○×	-30	××
	38	461	<-110	○×	<-110	○×
	39	587	-71	○○	-15	××
	40	618	-92	○○	-11	××

【0049】表3からわかるように、No. 1～32の本発明例の鋼は、APIの80ksi級（0.2%耐力：551MPa以上）の高強度を有しながら、母材および溶接部の靱性と耐食性がともに良好であった。

【0050】これに対し、No. 33～35の従来鋼（2相ステンレス鋼）は、いずれも強度が低く、靱性も劣っているだけでなく、耐食性も不十分で、特に溶接部の耐食性が劣っていた。

※【0051】また、化学組成が本発明で規定する範囲を外れるNo. 36～40の比較例の鋼のうち、No. 36の鋼は強度と靱性は良好なものの、Mo量が少ないために、耐食性が2相ステンレス鋼より劣っていた。No. 37の鋼はMo量が多すぎるうえに、Coを含まないためにδフェライトが生成し、強度と靱性が低いだけでなく、耐食性も劣っていた。No. 38の鋼は本発明で規定する量のMoとCoを含むものの、Ni量が本発明で規

定する範囲の上限を外れて過剰なために、Ms点が室温付近まで低下した。その結果、残留オーステナイト相が多く、韌性はすこぶる良好なものの、強度が低く、耐食性も劣っていた。No. 39~40の鋼はCまたはNの量が本発明で規定する範囲の上限を超えて過剰なために、母材の強度、韌性、耐食性は良好なものの、溶接部の韌性が極めて悪いのに加え、耐食性も劣っていた。

【0052】なお、上記の試験結果は、板材を対象とした結果であるが、試験材が鋼管や形鋼および棒鋼などであっても同様の結果が得られることはいうまでもない。

【0053】

【発明の効果】本発明のマルテンサイト系ステンレス鋼

は、高強度かつ高韌性でありながら高価な2相ステンレス鋼に勝る耐食性を有している。このため、従来は2相ステンレス鋼の使用が必須とされていた部分に用いることができ、高強度であることから部材の薄肉化が図れ、材料の使用量が少なくて済むので、2相ステンレス鋼を用いる場合に比べ、結果的に安くつく。また、機器装置の軽量化も図れる。

【0054】また、本発明鋼は、母材だけでなく、溶接部の性能も良好であり、油井管に限らず溶接して使用されるフローラインやラインパイプなどの用途に用いて極めて有効である。